

Amendments to the present title, specification and abstract:

Please substitute the following amended Title for the Title beginning on page 1 at line 1:

METHOD OF MAKING CARBON FIBER-CARBON MATRIX
REINFORCED MELT-INFILTRATED CERAMIC MATRIX COMPOSITES

Please substitute the following amended paragraph for the paragraph beginning on page 1, line 14:

—The invention relates in general to carbon fiber-carbon matrix reinforced ceramic composites and the production of such composites. —

Please substitute the following amended paragraph for the paragraph beginning on page 4, line 17:

—A low temperature chemical vapor deposition method for the formation of dense protective coatings of materials such as titanium dioxide, zirconium dioxide, hafnium dioxide, tantalum oxide, alumina, and the like on carbon fibers within a bundle of carbon is disclosed in Zinn et al. Serial No. 09/979,929 filed November 27, 2001, now U.S. Patent No. 6,921,707, and assigned to the same assignee as this application. Such protective oxide coatings are well suited to protecting the carbon fibers from reaction with molten materials in melt infiltration operations. —

Please substitute the following amended paragraph for the paragraph beginning on page 6, line 1:

—A preferred embodiment of the carbon fiber-carbon matrix reinforced ceramic composite according to the present invention comprises a carbon fiber-carbon matrix composite reinforcement embedded within a ceramic matrix, and a method for

producing such a reinforced ceramic composite. The ceramic matrix does not penetrate into the carbon fiber-carbon matrix composite reinforcement to any significant degree. The carbide matrix is a solid carbide of at least one metal having a melting point above about 1850 degrees centigrade. At least when the composite is intended to operate between approximately 1500 and 2000 degrees centigrade for extended periods of time the solid carbide with the embedded reinforcement is formed first. Molten silicon is then diffused into the carbide. The molten silicon diffuses preferentially into the carbide matrix but not to any significant degree into the reinforcement. Where the composite is intended to operate between approximately 2000 and 2700 degrees centigrade for extended periods of time such diffusion of molten silicon into the carbide is optional but not essential. —

Please substitute the following amended paragraph for the paragraph beginning on page 6, line 15:

—The carbon fiber-carbon matrix composite reinforcement comprises bundles of carbon fibers, for example, tows, in a carbon matrix. The individual fibers in each bundle are preferably coated to protect them from oxidation and or to permit them to slip relative to the carbon matrix. Typical coatings include carbides, nitrides, carbon, metallic oxides, and the like. —

Please substitute the following amended paragraph for the paragraph beginning on page 6, line 20:

—The ceramic matrix generally comprises a ~~metallic~~ metallic carbide composition. The metal carbide composition is tailored to the particular end use to which the reinforced ceramic composite is to be put. Typically, the metal carbide composition does not have a uniform composition throughout. The embedded carbon

fiber-carbon matrix composite reinforcements are preferably surrounded by metallic carbide layers or sheaths in which the ratio of metal to carbon is either carbon rich or near stoichiometric. The spaces between the reinforcement sheaths can be metal rich, silicon rich, or have about the same composition as the sheaths. Preferably, the carbide regions between the sheaths are metal rich so as to provide a more ductile and crack free ceramic. It has been found that the metal carbide layers or sheaths around the reinforcements protect them from attack by molten silicon. These sheaths are formed before the composite is exposed to molten silicon. Even though molten silicon is very aggressive in diffusing into carbon and in converting carbon to silicon carbide, it has been found that the preformed stoichiometric or carbon rich carbide sheaths adequately protect the carbon-carbon composite reinforcement from attack by the molten silicon. —

Please substitute the following amended paragraph for the paragraph beginning on page 8, line 9:

—The present invention provides its benefits across a broad spectrum of carbon fiber-carbon matrix reinforced ceramic composites. While the description which follows hereinafter is meant to be representative of a number of such applications, it is not exhaustive. As those skilled in the art will recognize, the basic methods and apparatus taught herein can be readily adapted to many uses. It is applicant's intent that this specification and the claims appended hereto be accorded a breadth in keeping with the scope and spirit of the invention being disclosed despite what might appear to be limiting language imposed by the requirements of referring to the specific examples disclosed. —

Please substitute the following amended paragraph for the paragraph beginning on page 8, line 20:

—Fig. 1 is an enlarged view (220 times) of a cross-section of a carbon fiber-carbon matrix reinforced ceramic matrix composite of the invention showing dark carbon fiber-carbon matrix composite reinforcements surrounded by sheaths of near stoichiometric zirconium carbide with a zirconium rich ceramic matrix extending between the sheaths. —

Please substitute the following amended paragraph for the paragraph beginning on page 9, line 1:

—Fig. 2 is an enlarged view (30 times) of a cross-section of the same carbon fiber-carbon matrix reinforced ceramic matrix composite shown in Fig. 1. —

Please substitute the following amended paragraph for the paragraph beginning on page 14, line 6:

—Preforms are prepared based on the desired configuration of the finished composite. The processing according to the present invention is such that the configuration of the preform can be maintained throughout so it is possible to make finished composites in near net shapes. Preforms can be made in substantially any desired shape and to preforms with non-uniform sections. The interface coating, particularly low temperature ultraviolet chemical vapor deposition applied oxides, can be applied to substantially any shape and to sections that are up to an inch or more thick. The carbon infiltration steps are likewise very tolerant of shape, size, and thickness variations. The melt infiltration proceeds by capillary action and gravity (when the infiltrant is placed above the preform) so this step is likewise very tolerant

of shape, size, and thickness variations in the preform. This greatly expands the possible applications for composites made according to the present invention, and reduces the need for extensive, expensive, and difficult machining operations on the completed composite. For example, a braided preform combustion chamber was prepared. This preform had a wall thickness of about 0.125 inches. The fiber volume in the braid was about 35 percent. Due to reproducible expansion of the perform during processing, the wall thickness of the end parts tended to be approximately 0.160 inches, which drops the fiber volume to approximately ~~25 volume~~ 25 volume percent in the finished composite part. —

Please substitute the following amended paragraph for the paragraph beginning on page 15, line 3:

—The initial metal infiltrant reacts with the sacrificial carbon around the fiber bundles to form a solid carbide matrix between the fiber bundles. The high melting point metals, mixtures, and alloys that are useful for this purpose, and particularly zirconium and hafnium apparently do not infiltrate or diffuse to any significant degree into the carbon fiber-carbon matrix composites that make up the reinforcements in the ceramic matrix. Silicon, by contrast, very aggressively diffuses directly into the solid carbide matrix and readily infiltrates into any open voids in the ceramic matrix. The amount of metal that is required to form a particular metal carbide matrix is generally determined by reference to the void volume of the carbon impregnated preform. Where the metal is placed above the preform and flows down into it, the amount of metal provided is preferably no more than approximately 15 to 25 volume

percent more than the void volume in the preform. This is economical of valuable refractory metals and it permits control over the amount of metal in the preform. The metal appears to distribute itself substantially ~~uniformly~~ throughout the preform. Within the preform the metal appears to react substantially stoichiometrically with the sacrificial carbon in the regions immediately adjacent to the fiber bundles. In the voids between the bundles of fiber the metal tends to form carbides that are metal rich. The presence of excess metal in what was previously void space does not appear to significantly limit the maximum temperature at which the composite can be used. For example, zirconium carbide matrix composites with zirconium rich regions have been successfully used at temperatures of nearly 2400 degrees centigrade, well above the 1855 degree melting point of zirconium. Such excess metal lends ductility and gas imperviousness to the composite. The volume of Zr introduced into the perform is typically 40-60 percent of the perform volume. The part is contained within an inductively heater graphite furnace (6-8 inches in diameter by 12 inches long), which is contained within a quartz vacuum chamber (10-12 inches in diameter by 4 feet long) with a pressure of less than about 5 torr, under 500 cubic centimeters per minute of argon and 1000 cubic centimeters per minute of of hydrogen during heatup. Heat up typically requires 30-200 min. Typically the maximum temperature is about 25 to 100 degrees centigrade above the melting point of the infiltrant metal. The system is held at this temperature for about 10 to 20 minutes. Typically it requires about 5 hours to reach a temperature below 200 degrees centigrade. During cool down the preform is kept under a blanket of argon at as flow rate of about 1000 cubic centimeters per minute of argon alone. —

Please substitute the following amended paragraph for the paragraph beginning on page 16, line 14:

—Molten silicon readily diffuses into a solid carbide matrix. It has been found that this diffusion can be enhanced if the carbide at the surface of the work piece is first lightly ground to remove a few thousandths of an inch (less than about 0.010 inches). The presence of a near stoichiometric layer or sheath of metal carbide around the bundles of fiber has been found to substantially inhibit the diffusion of the molten silicon into the fiber bundles. The volume percent of silicon in the ceramic matrix between the carbon fiber-carbon matrix composite reinforcement depends on the application, but is generally less than 50, and preferable from about 1 to 20 volume percent. After silicon infiltration the preform work piece typically exhibits from about 1 to 5 volume percent porosity. A greater concentration of silicon appears to exist at the infiltrated surface than in the center of the wall thickness. It appears that the carbon fiber-carbon matrix composite reinforcement in such a matrix promotes greater strength for a given fiber volume relative to conventionally carbon fiber-silicon carbide composites. —

Please substitute the following amended paragraph for the paragraph beginning on page 17, line 20:

—Within the finished carbon fiber-carbon matrix reinforced ceramic composite the fiber volume ranges from approximately 20 to 50 volume percent of the entire composite. The uncombined carbon (generally in the form of a pyrolytic carbon matrix

within the fiber bundles) generally ranges from about 10 to 25 volume percent. The metal, including silicon, in the completed composite (whether free or combined in a carbide) generally ranges from about 30 to 60 volume percent. Generally, where complete conversion of the metal to carbide is desired, it is preferred to provide approximately a 10 to 20 percent excess of carbon over the stoichiometric amount required to react with the metal infiltrant. Stoichiometric zirconium carbide, for example, is about 78 volume percent zirconium and 12 volume percent carbon. —

Please substitute the following amended paragraph for the paragraph beginning on page 18, line 7:

—The nature of the finished composite is apparent from Figs. 1 and 2. A preform was braided from 7 micron diameter carbon fibers in tows of about 3000 fibers each, coated with zirconium dioxide in a low temperature ultraviolet chemical vapor deposition process, infiltrated with pyrolytic carbon using chemical vapor infiltration techniques to where there was less than about 5 volume percent void space within the tows, and infiltrated with about 15 volume percent excess molten zirconium to where there was less than about 5 volume percent void space within the entire composite. The resulting ceramic carbide had about 25 volume percent of carbon fibers. The resulting carbon fiber-carbon matrix composite reinforced ceramic carbide composite was sectioned and photographed. Copies of the resulting photographs appear as Figs. 1 and 2. The black elongated regions are carbon fiber-carbon matrix ~~composites~~ composite reinforcements. The dark sheaths around the ~~carbon-carbon-composites~~ carbon fiber-carbon matrix composite reinforcements are

near stoichiometric zirconium carbide, as are the darker spots in the matrix between the ~~carbon-carbon-composites~~ carbon fiber-carbon matrix composite reinforcements. These are the areas occupied by a dense coating of pyrolytic carbon that encapsulated the fiber tows during the carbon infiltration step. The lighter colored regions between the encapsulating sheaths of zirconium carbide are zirconium rich zirconium carbide and zirconium metal. The lighter colored regions mark where the void space was at the time the zirconium infiltration step was commenced. The dense zirconium carbide sheaths show signs of microcracking, but the cracks do not extend into the more metal rich ceramic regions. The use of metal rich composite is preferred because of its increased toughness and reduced gas permeability as compared with stoichiometric carbide. Because the ~~carbon-carbon-composite-reinforcement~~ carbon fiber-carbon matrix composite reinforcements ~~retains its~~ retain their character the thusly reinforced ceramic composite is able to operate at much higher temperatures than would be the case if the ~~carbon-carbon-composite~~ carbon fiber-carbon matrix composite reinforcements were to be converted to silicon carbide. A second substantially similar composite was prepared. Approximately 0.005 to 0.010 inches of the composite were removed from its surface by grinding. The composite was heated in a furnace and contacted with molten silicon. Substantially all of the molten silicon diffused into the solid zirconium carbide ceramic leaving a silicon rich deposit on the surface of the composite. The silicon did not attack the ~~carbon-carbon-reinforcement~~ carbon fiber-carbon matrix composite reinforcements to any significant degree, but it was distributed throughout the metal rich and stoichiometric regions of the ceramic

carbide matrix. Substantially similar results are achieved by substituting hafnium for some or all of the zirconium. —

Please substitute the following amended Abstract for the Abstract beginning on page 27 at line 2:

— A method of making a carbon fiber-carbon matrix reinforced ceramic composite wherein the result is a carbon fiber-carbon matrix reinforcement is embedded within a ceramic matrix. The ceramic matrix does not penetrate into the carbon fiber-carbon matrix reinforcement to any significant degree. The carbide matrix is a formed in situ solid carbide of at least one metal having a melting point above about 1850 degrees centigrade. At least when the composite is intended to operate between approximately 1500 and 2000 degrees centigrade for extended periods of time the solid carbide with the embedded reinforcement is formed first by reaction infiltration. Molten silicon is then diffused into the carbide. The molten silicon diffuses preferentially into the carbide matrix but not to any significant degree into the carbon-carbon reinforcement. Where the composite is intended to operate between approximately 2000 and 2700 degrees centigrade for extended periods of time such diffusion of molten silicon into the carbide is optional and generally preferred, but not essential. —